MCI request number: 6174.1

PROJECT TITLE: Anchorage Loan Project

Object: Grass Bag

Accession no.: 

Catalog no.: E032971

Geographic region: Alaska, Yup’ik

Materials: twined grass

Date: collected 1878 by Edward W. Nelson

Sample: white-brown surface residue

Requested by: Kim Cullen Cobb, Conservator; Greta Hansen

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Unit: NMNH

Analyst: Lynn Brostoff

Date of request: 1/16/08

Dates of analysis: 1/29/08

Report author and date: Lynn Brostoff, 5/17/08

Requested analysis

FTIR analysis of sample.

Purpose of analysis

Ethnographic objects collected during the late 1800s were routinely treated with a wax and gasoline bath to inhibit pest activity. They also may have been treated with British Museum leather dressing as part of conservation. This grass bag may have been subjected to one or both of these types of treatments. Identifying the surface coating will assist in
subsequently devising a conservation treatment strategy to humidify and reshape the bag; conservation treatment will be undertaken by ACL conservators.

Summary of results

FT-IR analysis indicates that the fine, buff-colored particulate matter that has appeared over most of the basket surfaces is beeswax, which may either be the product of a former wax/gasoline bath treatment, or have crystallized out from previous application of British Museum leather dressing. The material thus appears to have formed as a result of a former conservation treatment and environmental conditions/aging.

FT-IR Analysis Report

Introduction

Electromagnetic radiation in the mid-infrared (IR) region, where wavelengths correspond to frequencies of about 4000-400 cm\(^{-1}\) (or wavenumbers), is especially useful for probing the molecular structure of organic and organo-metallic substances. Photon energies associated with this part of the spectrum are not large enough to excite electrons, but may induce vibrational excitation in molecular groups. At ordinary temperatures, molecules experience a wide variety of vibrational motions, characteristic of their component atoms. This is due to the nature of covalent bonds, which act much like stiff springs that can be stretched and bent. If the frequency of the input radiation matches the vibrational frequency of the molecular group, then radiation will be absorbed, causing a change in the amplitude of molecular vibration. The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms. In order for a vibrational mode in a molecule to be IR active, however, it must be associated with a net change in the permanent dipole, i.e., the electronic charge distribution, in a molecular species. For example, the atoms in a CO\(_2\) molecule can vibrate by both symmetrical and asymmetrical stretching, which induces tiny changes in inter-atomic distances along the bond axes. However, symmetric stretching vibrations in this case have no change in the electronic dipole moment, and are therefore not detectable, or “active,” using infrared radiation. In addition to stretching vibrations, molecules typically exhibit bending vibrations, including, scissoring, rocking, wagging and twisting, each of which potentially occurs upon excitation at a characteristic IR frequency. Thus, the frequency of individual IR-active vibrations can be associated with a particular type of bond in a particular molecular species or functional group.

The infrared spectrum of an individual sample is collected by passing a beam of infrared light into the sample, which may be prepared and mounted by various techniques. Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous). In all cases, examination of the transmitted or reflected light reveals how much energy was absorbed, i.e., lost, at each frequency where a vibration took place in the sample. This is
accomplished on MCI’s Thermo Nicolet 6700 Fourier transform infrared spectrometer (FTIR) by measuring all wavelengths at once, producing a transmittance, absorbance or reflectance spectrum that reveals absorption bands, or peaks, at characteristic IR frequencies.

Complex molecular structures and mixtures lead to more absorption bands and more complex spectra, usually with overlapping bands. The interpretation of infrared spectra involves the correlation of absorption bands in the spectrum of an unknown compound with the known absorption frequencies for types of bonds. Analysis of these absorption characteristics reveals details about the molecular structure of materials in the sample. Significant for the identification of the source of an absorption band are intensity (weak, medium or strong), shape (broad or sharp), and position (cm$^{-1}$) in the spectrum. Intensity is influenced by the magnitude of change in the dipole moment that takes place in that mode, and the associated energy involved in dissociation of the bond. It generally requires more energy to stretch (or compress) a bond than to bend it, so that stretching absorptions usually produce stronger peaks than bending. For example, absorption bands associated with carbonyl (C=O) bond stretching are usually very intense. When measured in absorbance units, total integrated intensity is also proportional to the concentration of a particular molecular species or chemical group.

Not all molecules are exactly the same, even those of the same substance. They will be moving differently, vibrating and rotating differently, and have different neighbors. Both absorption band position and shape are influenced by these factors, and in particular by variations in chemical environment in which a particular bond exists. Thus, absorption bands occur at slightly different wavelengths in different molecules. For example, conjugation and nearby atoms shift the frequency to a lesser degree. In addition, any significant quantity of a compound will contain a very large number of individual molecules, and each of these may be in a slightly different chemical environment, e.g., hydrogen bonded to a slightly different extent. Thus, IR absorptions will occur at varying frequencies for each of these bonds. The end result is that the IR peak, such as typically seen in the –OH stretching region, appears broadened, since it is an average of all these slightly different absorptions. Therefore, the same or similar functional groups in different molecules will typically absorb within frequency ranges.

While many infrared absorption bands are characteristic of types of functional groups, the complexity of infrared spectra in the 1450 to 600 cm$^{-1}$ region makes it difficult to assign all the absorption bands here; the unique patterns found in this part of the spectrum give rise to the term “fingerprint region.” Using spectral databases and reference materials, IR spectra may be used to confirm the identity of unknown compounds, based on the chemical groups present and patterns in the fingerprint region.

Attenuated total reflection (ATR) IR is a useful and convenient method for investigating the surfaces of solids and films by FT-IR. In this case, the infrared beam is passed through a prism or crystal so that it is internally reflected back from the face of the crystal. Depending on the angle of incidence of the radiation, and the ratio of the refractive indexes of the crystal and the sample medium pressed onto the crystal, total internal reflection may occur. In this case, an evanescent (i.e., vanishing) wave having the same frequency as the totally reflected radiation interacts with an absorbing sample material just beyond the sample/crystal interface, leading to an attenuation of IR beam, i.e., to absorption bands that originate from the first few microns into the substance. The actual depth of penetration of the evanescent wave into the sample may be calculated and depends on the
crystal medium, the angle of incidence, and the refractive indexes. The amount of absorption is dependent on the area and efficiency of contact. In addition, the effective penetration of the evanescent wave into the sample is a direct function of the wavelength of the radiation. This means that as the wavelength increases, bands get deeper relative to those in a transmission spectrum. Therefore, mathematical functions are performed on the data to correct for the wavelength dependency. For all ATR mathematical corrections, index of refraction of the sample material was estimated as 1.50 (unless otherwise known). The ATR accessory utilizes the bench DGTS detector, with a range of 4000 – 400 cm⁻¹.

Transmission FT-IR is also conveniently accomplished with very small samples by squashing the sample in a diamond anvil cell and then passing the IR beam through the microscope lens and condenser path, and through the sample/diamond crystal. The Nicolet microscope is used to accurately position the sample in the beam path, and apertures are used to limit the beam to the sample shape and size. Background subtraction is obtained by passing the IR beam through the same aperture setting on a clean area of the diamond crystal face. Spectra are obtained in % transmission, and no corrections are necessary. The FT-IR microscope utilizes an MCT detector cooled with liquid nitrogen, with a range of 4000 – 500 cm⁻¹.

**FT-IR Methodology**

I. **Instrumental parameters**

Instrument: Thermo Nicolet 6700 Fourier Transform Infrared Spectrometer; Centaurus Microscope

Detector: DTGS for ATR; MCT for FT-IR microscope

Sampling accessory:

(a) Golden Gate ATR (Attenuated Total Reflection) with Diamond crystal, single bounce, 45º, mounted directly onto the spectrometer bench compartment.

(b) Diamond Anvil Cell, mounted under FT-IR microscope

Resolution: 4 cm⁻¹

Aperture: 150 (open) for ATR; variable for FT-IR microscope

Number of scans: 64-128

Purge: none

Corrections: ATR correction, with baseline correction, as needed, using 1.5 as sample refractive index.

II. **Sampling**

Sampling was conducted by the analyst on the grass by removing tiny amounts of residue with a dissecting needle or scalpel, under magnification, as appropriate. Particulate matter on the grass basket was picked off from several locations, including both inside and outside surfaces. See attached documentation for sampling locations.

Prior to analysis, all samples were examined under magnification and separated, if necessary, into chunks or relatively homogeneous material.

For all ATR-FT-IR analyses, particles of the samples were placed onto the diamond ATR crystal with a backing of clean aluminum foil to cover any areas of the crystal that did
Results and Discussion

Grass Basket efflorescent material

The residue on the basket appears to the naked eye to be a type of efflorescence, finely dispersed over most of the surfaces and in the interstices of the basket. The material appears as fine, whitish crystalline-looking particles. Samples were picked off in several places, as shown in the attached documentation. Under magnification, samples removed from the basket appear as small brownish chunks; the chunks are hard, and have dark specks in some locations. Some fiber residue that had fallen off of the basket was also examined. Under magnification, glassy, dark brown particles can be also seen attached to the fibers. Both the fibers and the sampled brown particulate matter were analyzed by ATR-FT-IR. The spectra are shown below, in Fig. 1.

Comparison of spectra taken from the fiber (A) and brown particulate matter (B) (Fig. 2) reveals that the fiber spectrum is a composite of cellulosic material and the material making up the brown particulate matter. This confirms observations that the brown glassy material coating the fibers matches with that which has effloresced more discreetly over the basket surfaces.
As shown in Figure 2, below, the spectrum of the brown particulate material matches very well with beeswax. The spectrum also compares well with a dried sample of British Museum (BM) Leather Dressing, which was found in solution, stored in the organic laboratory at MCI. A traditional recipe, which most likely was used to make up this dressing, is composed of lanolin, cedarwood oil, beeswax, and hexane. Beeswax would thus represent about 17% of this dried formulation.

Figure 2: Overlay of ATR-FT-IR spectra of a) basket particulate matter, b) paraffin wax, c) reference spectrum of beeswax, and d) dried British Leather Museum dressing.

It is clearly seen that despite the relatively small proportion of beeswax in the dressing, it dominates the FTIR spectrum. The lanolin and cedarwood components add primarily to the intensity of the peaks just below 3000 wavenumbers, due to methylene absorption, and influence the shape of peaks near 1735, 1462 and 720. In the latter case, peak splitting is not as evident as in the beeswax. Splitting in this peak is known to be associated with a vibration of the wax crystal.

FT-IR analysis thus confirms that the particulate matter formed discretely over the surfaces, as well as on the fibers, is primarily associated with beeswax, which appears to have crystallized out from a former application in solvent or from BM leather dressing over time. In either case, FT-IR analysis indicates that the residue on the basket surfaces has most likely formed as a result of a former conservation treatment and environmental conditions/aging.

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Appendix I: Photodocumentation of Objects with Sampling Locations

Sampling location on grass basket, 2.

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